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EFFECT OF ELECTROLYTES ON THE VISCOSITY OF POTATO STARCH PASTES

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INTRODUCTION

A most important property of all starches is their ability to swell in hot water to form viscous liquids, or pastes. This property is utilized whenever starch is used as a thickening or gelling agent, a coating or sizing material, or an adhesive. Among the commercial starches potato starch swells the most, thereby giving the most viscous and unstable pastes, and is also the most variable. It is now evident that these distinctive qualities arise largely because potato starch is a polyelectrolyte. Its electrolyte properties are conferred by dihydrogen-orthophosphate groups in ester combination with the branched amylopectin fraction of the starch. Thus combined, the phosphate groups have substantially the same dissociation properties as the first and second hydrogens of ordinary phosphoric acid (1).

The phosphorus content of native potato starch is variable, but usually lies in the range 0.06–0.10%. This corresponds to one phosphate group to roughly 400 glucose residues in the whole starch, or to 300 residues in the amylopectin. At the normal potato starch pH of around 6.5, three-fourths of the phosphoric acid hydrogens are replaced by metal ions, principally potassium. When the starch is pasted its electrolyte groups ionize, leaving the carbohydrate with a negative charge. Repulsion of the negative amylophosphate ions greatly opens up the branched amylopectin molecules and increases their solvation. Compared with an electrically neutral starch this has the result that the pasted granules are larger and the starch paste viscosity is higher but sensitive to small concentrations of added electrolyte. Forty years ago Samec (2) noted that potato starch sols and pastes are electroviscous, and correctly associated the electroviscosity with the starch-phosphoric acid. Other notable reports on potato starch-electrolyte interaction have been made by Bungenberg de Jong (3); Ripperton (4), and Wiegel (5).

The cations of potato starch are easily exchangeable by others (6,7). In the experiments described here a series of such modified starches was

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prepared, with sodium, potassium, ammonium, hydrogen, and calcium as cations. The viscosity of pastes made from these starches was measured, and effects of pH and added electrolyte were observed. Viscosity and starch granule swelling were related by means of photomicrographs.

EXPERIMENTAL

Preparation of Modified Starches

Starting material was a high grade commercial potato starch (Aroostocrat Brand). In this, as in commercial potato starches generally, the original potassium had been largely replaced by calcium during manufacture. Exploratory experiments, in which the natural potassium starch was prepared from potatoes in the laboratory, indicated no advantage over the commercial starch. To make the cation modified starches, kilogram portions of the parent starch were soaked 2 hours in 0.5 *N* solutions of either sodium, potassium, ammonium, calcium, and hydrogen chlorides, or in 3.8% "sodium hexametaphosphate" (Calgon, used as the grade, Medi-Calgon). The starches were washed repeatedly with distilled water, then with 95% ethanol, absolute methanol, and were dried at room temperature in a current of filtered air. For all but the hydrogen starch the conductivity of 1% pastes was equivalent to that of $1 \text{ to } 3 \times 10^{-4}$ *N* KCl. This magnitude is appropriate for the starch-phosphoric acid and associated cations, and suggests that any residue of uncombined electrolyte was negligible in amount. For the hydrogen starch, owing doubtless to the extraordinary mobility of hydrogen ion, the paste conductivity was equivalent to 8×10^{-4} *N* KCl. From the phosphorus content of the hydrogen starch, 0.09%, it may be computed that the (combined) phosphoric acid concentration in the 1% paste was 3×10^{-4} molar. The paste pH was 3.6, corresponding to a hydrogen ion concentration of 2.5×10^{-4} *N*. The hydrogen starch, then, likewise seemed free from appreciable amounts of foreign electrolyte. It was considered that potato starch could not be electrodialed free from electrolytic contaminants without spoiling it for the intended application. For as the metal ions are replaced by hydrogen ions during the necessarily prolonged electro dialysis the pH drops to about 3.5, so hydrolysis or at least damage to granule structure is to be anticipated.

Preparation of Starch Pastes

For viscosity measurements pastes were prepared at two concentrations, 0.4% and 1%. To make a 0.4% paste, 4.5 g. of distilled water was added to a 0.4 g. starch sample, and to this slurry 95 g. of distilled water at 100° was added almost instantaneously. The paste was swirled, kept at 100° without further agitation for 30 min., then transferred to a water bath at 30° for at least $\frac{1}{2}$ hour before filling the capillary viscosimeter,

which was kept and used in the same 30° bath. The 1% pastes were made analogously, with slurries composed of 1 g. of starch and 4 ml. of water. After addition of the boiling water the paste was put in a 90° bath for about 5 min. The viscosimeter was then filled and viscosities at 90° measured over periods of 2 to 4 hours.

Viscosity Measurement

Starch pastes are non-Newtonian fluids. So marked is their structural viscosity that Ostwald type viscosimeters even of the same ASTM series—and thus with about the same capillary diameter—cannot be used interchangeably as they can for ordinary liquids. To further illustrate how sensitive starch pastes are to rate of shear, the apparent viscosity of both potato and corn starch pastes was roughly ten times higher when measured with a Brookfield (torsional) viscosimeter, using the most appropriate rotor and rotational speed, than with a capillary viscosimeter. All the viscosities reported here were measured in a single ASTM series 300 pyrex viscosimeter, whose calibration constant was 0.1887. Flow times ranged from 6 sec. to almost half an hour. Over-all reproducibility of paste viscosity observations was ordinarily $\pm 5\%$ or better. Viscosity lowering by electrolyte dissolved from the viscosimeter was apparently unimportant for freshly made pastes, since decreases in flow time with less than 10^{-4} *N* added electrolyte were easily measured both with the Ostwald viscosimeter and with the Brookfield viscosimeter, whose parts in contact with the starch paste were made of stainless steel. An effect possibly assignable to electrolyte dissolved from the glass capillary was the viscosity decrease on standing at 90° shown by pastes made from several of the regenerated potato starches. This decrease was considerably greater than Wiegel (5,8) observed with a silica viscosimeter and more like that observed with a viscosimeter made from Thuringia glass. Alternatively, the pronounced viscosity decrease may simply be an expression of the conditions of pasting, since Wiegel also noted high initial but unstable viscosity when pasting was done rapidly (5).

RESULTS

Figure 1 shows the variation of viscosity with duration of pasting at 90° for four 1% pastes. Viscosity is expressed as "apparent centistokes," computed as the product of flow time and viscosimeter constant for normal fluids. The parent commercial potato starch (Curve 3) had a low paste viscosity which fell only slightly during three hours. The derived sodium starch (Curve 2) had an initial viscosity over ten times as high. The viscosity fell rapidly, from 280 to 60 in an hour and a half, but during the period of observation was always more than three times that of the parent starch. "Calgon starch" (Curve 1) had an even higher viscosity

than the sodium starch, and was similarly unstable. Pasting the Calgon starch in 0.00125 *N* CaCl₂ reduced the viscosity to a very low constant value (Curve 4) not much greater than that for water. Other starches and other electrolytes at equivalent concentration gave comparably short flow times (10 sec.). A distilled water paste of the Calgon starch, initially clear and viscous, was made 0.0025 *N* in Na⁺. Instantly the paste became cloudy and its viscosity dropped to a stable value of 3. The granule sacs of the original paste were shrunk in the electrolyte, but because of their

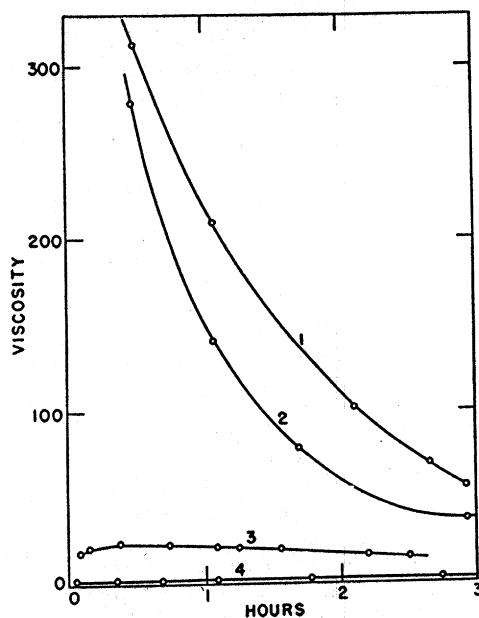


FIG. 1. Viscosity of 1% potato starch pastes at 90°C. 1. Calgon-treated starch. 2. Sodium starch. 3. Parent commercial starch. 4. Calgon-treated starch pasted in 0.00125 *N* calcium chloride. Viscosity is expressed as "apparent centistokes."

irregular form a quantitative estimate of the magnitude of the shrinkage was not attempted (9).

The 0.4% pastes at 30° were much more stable with respect to time, and the single viscosity values given in Table I are characteristic for the particular samples of modified starches. The hydrogen starch paste was measured at its natural pH, 4.2, whereas the pH of the other starches was adjusted when necessary to 6.7 by means of 0.01 *N* KOH, thereby increasing the electrolyte concentration by a maximum of 4×10^{-5} *N*. The Calgon starch paste viscosity was more than twice as high as that of any other starch. A pure calcium starch gave a higher viscosity than the parent commercial starch, presumably because the commercial starch

was contaminated with a small amount of soluble electrolyte and this depressed the viscosity. Potassium chloride at 10^{-4} *N* concentration reduced the potassium starch viscosity from 25.7 to 7.0. Borax, which at higher starch concentrations increases viscosity (10), lowered the viscosity of dilute potato starch pastes just as any other electrolyte. Microscopic examination showed that the hydrogen starch granules were largely destroyed in the pasting at pH 4. This leads to the inference that the major reason for the low paste viscosity was the diminished size of the flowing units due to solution or granule breakup rather than granule swelling hindered by electrolyte.

TABLE I
Viscosity of Starch Pastes at 30°C.

	pH	Viscosity "apparent centistokes"
Potato starches, 0.4%		
"Calgon"	6.7	100.3
Ammonium	6.7	38.7
Sodium	6.7	31.5
Potassium	6.7	25.7
Calcium	6.7	12.5
Parent commercial	6.7	8.5
Hydrogen	4.2	3.0
Potassium, in 10^{-4} <i>N</i> KCl	6.7	7.0
Potassium, in 10^{-4} <i>N</i> CaCl ₂	6.5	5.9
Potassium, in 10^{-3} <i>N</i> KCl	6.5	2.5
Sodium, in 10^{-3} <i>N</i> Na ₂ B ₄ O ₇	9.5	2.5
Sodium, in 2×10^{-3} <i>N</i> NaCl	9.5	2.1
Waxy maize starch, 1%	5.7	6.6
Waxy maize starch, 1%	10.0	16.0
Waxy maize starch, 1%, in 10^{-3} <i>N</i> NaCl	6.2	8.3
Tapioca starch, 1%	6.0	7.3
Tapioca starch, 1%	10.0	13.2
Tapioca starch, 1%, in 10^{-3} <i>N</i> NaCl	5.4	6.9

Figure 2 shows the large effect of pH on the viscosity of sodium starch pastes. The pH was changed by adding KOH or HCl to the pastes after cooling to 30° in order to minimize granule damage and hydrolysis. The pH-viscosity curve rises almost symmetrically from values near 4 at pH 4 and 12 to a maximum viscosity of 40 at pH 8.4. At pH 2 the starch is practically unionized and the paste viscosity is nearly as low as that of water. As the pH rises, starch ionization increases, and with it the viscosity. According to Briggs and Hanig (1) the second hydrogen of amylophosphoric acid is neutralized at pH 8.75, but at higher pH alkali continues to react with starch, possibly by combining with the slightly acidic glucoside hydroxyls. Further development of charge by this mechanism

could conceivably increase the potato starch electroviscosity still more. Experience showed instead that the viscosity decreased markedly above pH 8.4. To raise the paste pH from its normal value to 10, the additional cation introduced as KOH amounted to roughly $5 \times 10^{-4} N$, and this induced the viscosity decrease expected of $5 \times 10^{-4} N$ NaCl or other electrolyte.

Negative ionization of glucoside hydroxyls and correspondingly increased viscosity apparently was realized with 1% pastes of waxy maize and tapioca starches. At normal pH these are nonelectrolytes and have nearly the same viscosity in $10^{-3} N$ NaCl as in water, but the viscosity

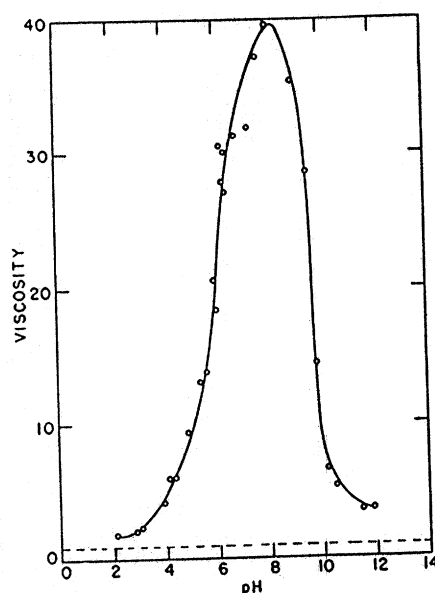


FIG. 2. Effect of pH on the viscosity of 0.4% sodium starch pastes at 30°. The dotted line represents the viscosity of water. Viscosity is expressed as "apparent centistokes."

of both starches doubled as the pH was raised from 6 to 10 (Table I). Equivalent behavior expected of potato starch pastes was masked by the predominant electroviscous effect of the phosphate ions.

Changes in granule appearance on pasting in water and in dilute electrolytes are shown in the photomicrographs of Figs. 3 and 4. Figure 3a is unpasted commercial potato starch. All the unpasted potato starches had a similar appearance. Figures 3b, c, and d, made at the same magnification, are, respectively, sodium starch pasted in distilled water, sodium starch pasted in $0.001 N$ $CaCl_2$, and ammonium starch pasted in distilled water. All were pasted $\frac{1}{2}$ hour in a boiling water bath at 0.4% concentration, and were then diluted to a concentration suitable for micrography

with 8 volumes of a saturated solution of iodine in distilled water. Iodine stains preferentially the amylose component of the starch. It stains the granule sacs, the liquid contents and the suspending liquid, showing the presence of amylose in all, and reveals much more detail in the structure than is possible without the stain. Iodine has the important disadvantage, however, that while it stains it also partially de-swells the pasted gran-

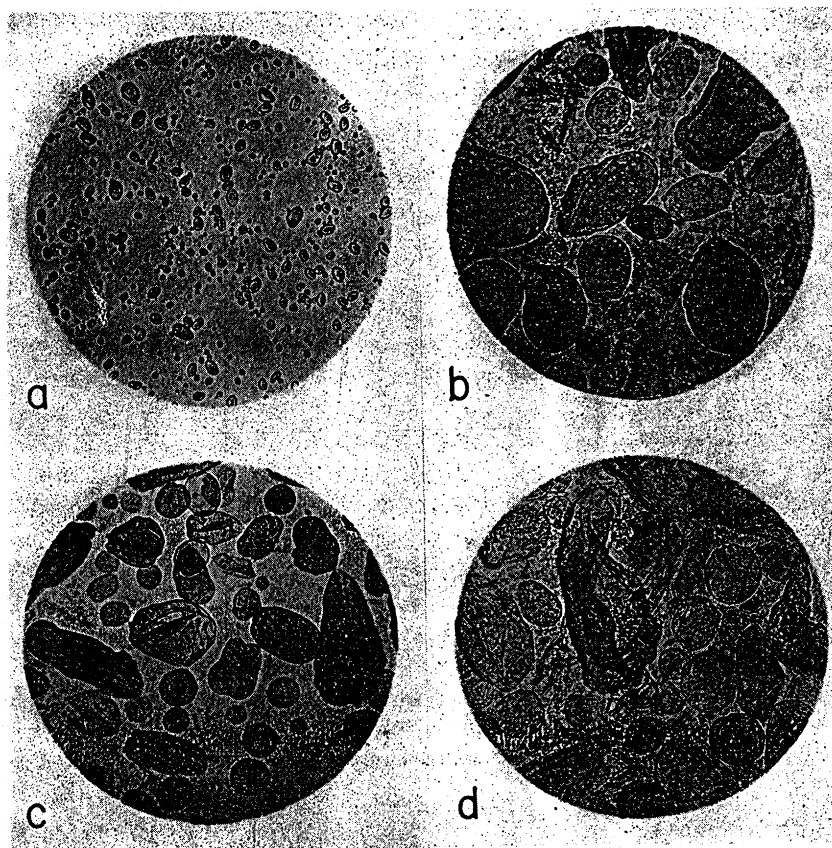


FIG. 3. Photomicrographs of potato starches. (a) Commercial starch, not pasted. (b) Sodium starch pasted in water, diluted with I₂ solution. (c) Sodium starch, pasted in 0.001 *N* CaCl₂, diluted with I₂ solution. (d) Ammonium starch, pasted in water, diluted with I₂ solutions. Magnification 36 ×.

ules; the viscosity of pastes diluted with iodine solution is considerably less than the viscosity of pastes diluted with water alone, and the average granule size is smaller. It may be surmised that the action of the iodine solution is twofold: action of electrolyte in the iodine solution on the amylopectin, and action of the iodine itself in forming the helical complex with amylose (11). Both would have the effect of shrinking the carbo-

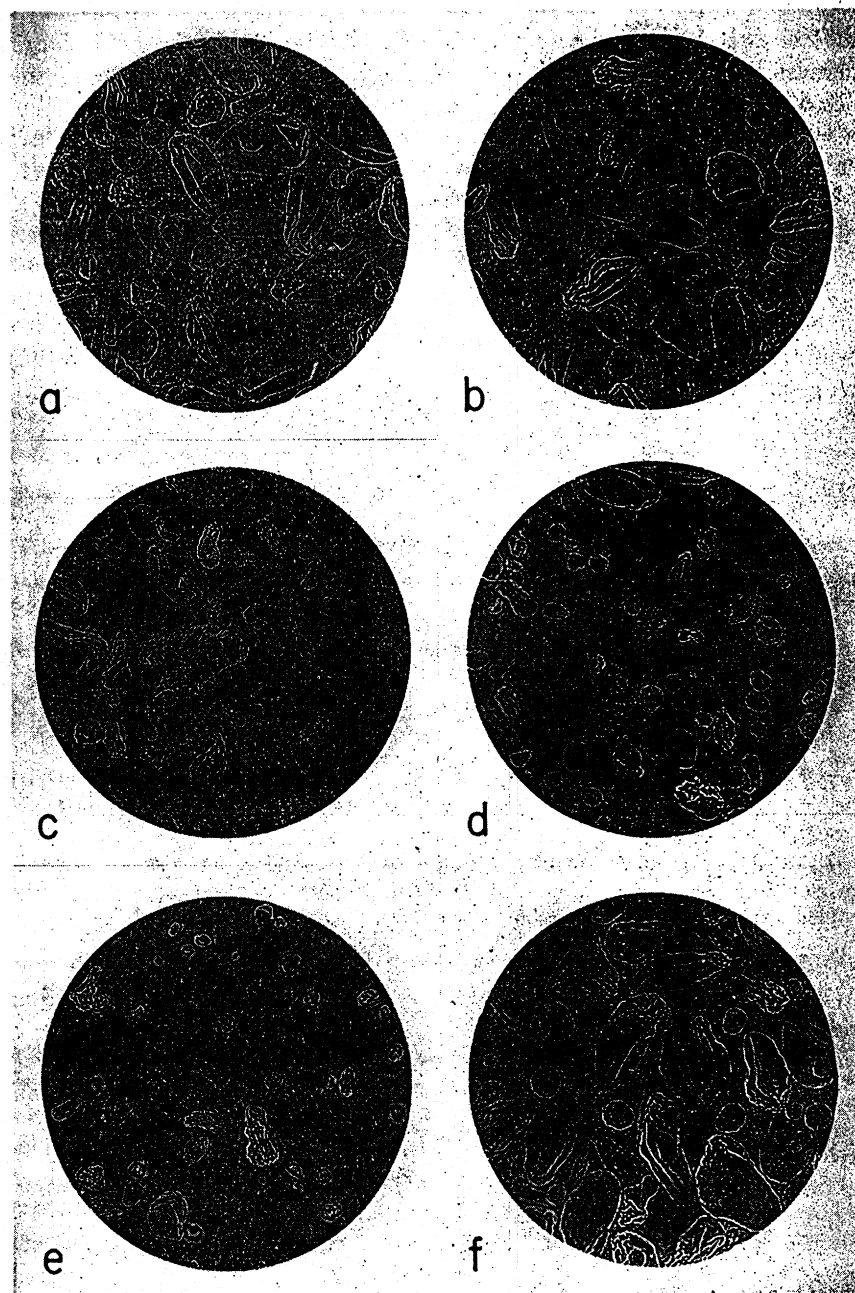


FIG. 4. Photomicrographs of pasted potato starches; 0.008% concentration; not stained. (a) Sodium starch. (b) Calcium starch. (c) Sodium starch pasted in 0.001 *N* NaCl. (d) Sodium starch pasted in water, then made 0.001 *N* in NaCl. (e) Sodium starch pasted in 0.001 *N* $\text{Pb}(\text{NO}_3)_2$ at pH 6.1. (f) Calgon starch. Magnification 29 \times .

hydrate. For photomicrography the stained pastes were contained in a cell 220 μ thick. A comparison of Fig. 3*b*, *c*, and *d* with *a* shows the large increase, amounting to five- or tenfold, in linear dimensions of the granules on pasting. The smaller pasted granules are approximately circular in cross-section, whereas the larger granules are progressively irregular, and at the onset of collapse the sacs develop a system of wrinkles or folds. It is obvious that the extent of swelling in CaCl_2 solution is considerably less than in water.

In Fig. 4 the photomicrographs were made at 0.008% concentration. Since many swollen granules are 100 to 200 μ or more in at least one dimension, a cell 2 mm. thick was used to avoid distortion or artifact formation due to confining the granules. The starch was not stained, with the result that at sharpest focus the contrast in the images was so slight

TABLE II
Analytical Data on the Potato Starches

Starch	Na	K	Ca	P	SiO ₂	Ash	pH of 1% paste
	%	%	%	%	%	%	
1. Commercial (parent)	0.007	0.01	0.063	0.108	0.012	0.36	6.5
2. Sodium	0.07	0.002	0.01	0.104	0.013	.32	6.6
3. Calgon	0.06	—	0.005	0.088	0.02	—	5.8
4. Potassium	—	0.11	—	—	—	—	6.6
5. Calcium	—	—	0.09	—	—	—	6.9
6. Hydrogen	0.001	0.001	0.002	0.090	0.014	0.04 ^a	3.7
7. Laboratory ^b	0.003	0.07	0.006	0.096	0.007	0.29	6.1

^a Ash with magnesium acetate, 0.19%.

^b Contained also 0.04% R_2O_3 ; several other starches contained 0.03 to 0.04%; hydrogen starch contained 0.01%. Laboratory starch prepared from potatoes using only distilled water, and air dried at room temperature.

as to be unuseable. The photomicrographs were purposely made slightly out-of-focus. They thus show only the granule outlines and the major folds. Sodium and Calgon starches pasted in distilled water (4*a* and *f*) swell greatly, calcium starch (4*b*) somewhat less, and sodium starch pasted in 0.001 *N* NaCl (4*c*) very much less. The sodium starch of Fig. 4*d* was first pasted in distilled water, so that the granule swelling was comparable with 4*a*. Sodium chloride then added to a final concentration of 0.001 *N* instantly shrunk the granules, as is shown in 4*d*. Pasting the sodium starch in 0.001 *N* $\text{Pb}(\text{NO}_3)_2$ produced the least granule swelling of all (4*e*). It may be noted from Fig. 4 that smooth spherical granules are decidedly the exception.

Analytical data on some of the starches are given in Table II. In general the data agree rather well with the much more extensive analyses of Tryller (6). The principal differences are in the SiO_2 and R_2O_3 contents.

Tryller found 0.04 to 0.09% SiO_2 , whereas we found 0.007 to 0.02%; and Tryller found 0.01% R_2O_3 whereas our analyses showed about 0.04%. Noteworthy is the small total content of metal ions and ash in the hydrogen starch. The intrinsic metal and ash content of potato starch is of course variable with pH, owing to different extent of neutralization of the two replaceable hydrogens of the starch phosphoric acid. The Calgon starch contained no unusual amount of either sodium or phosphorus on which an explanation of its abnormal paste viscosity could be based.

DISCUSSION

In a starch grain the linear amylose molecules and even the branches of the globular amylopectin molecules have a generally radial arrangement extending from the hilum to the surface. This arrangement, in effect, places the three hydroxyls of each glucose residue perpendicular to the radii. When starch is heated in water, hydration of the hydroxyl groups produces enormous tangential expansion. As a rule the granule expansion is so rapid and so great that most of the starch substance goes into the balloon-like envelope or sac (often momentarily hollow) filled with water that seeps through between molecules or lamellae, or cracks or breaks (12). In this interior water there must be a greater or lesser amount of dissolved amylopectin and amylose. For a $20\ \mu$ granule which on pasting becomes $200\ \mu$ in diameter, the computed sac thickness is only 330 A., even if it is assumed that all the starch substance goes into the sac. Owing to hydration and change in molecular shape the actual thickness is doubtless greater, but it is still very thin, correspondingly fragile and liable to be broken by simple dissolving away of the hydrated starch molecules if not by shear or other mechanical shock.

Paste viscosity correlates with the size of the flowing units that appear in photomicrographs to the extent that the more viscous pastes have the larger granules. It must be recognized, however, that the granules are considerably swollen, even in pastes whose viscosity is not much greater than the viscosity of water: such pastes as 0.4% sodium starch at pH 2, and 0.4% sodium starch in $10^{-3}\ N\ \text{Pb}^{++}$. In order that the granules might be separately visible, the photomicrographs in Figs. 3 and 4 were made at a concentration much lower than that used for the viscosity measurements. In the 0.4% and the 1% pastes the granules were presumably somewhat smaller than in the photomicrographs simply for lack of enough water to produce the maximum swelling. This is especially likely among the more viscous pastes, in which the swollen granules occupy practically the whole volume.

It is usually thought that the high viscosity of dilute potato starch pastes originates principally in the intact swollen granules, for when these are broken by vigorous stirring the viscosity drops abruptly. There may be, however, a substantial contribution to the paste viscosity by the dis-

solved starch substance. To illustrate, in one experiment the intact granules and the broken sacs were separated from a sodium starch paste by vacuum filtration through a Corning medium porosity sintered glass filter. About two-thirds of the volume was recovered in the filtrate before the filter clogged. Flow time for the original paste was 180 sec., for the filtrate, 88 sec., and for the filtrate after being made 10^{-3} *N* in KCl, 10 sec. The filtrate contained no particles visible in a microscope at 500 \times . When KCl was added to the filtrate it became much more opalescent, yet still there were no microscopically visible particles. These observations seem to indicate that starch substance dissolved from the granules and sacs occurs in units so large that by mutual hindrance as they move they develop considerable viscosity in the pastes aside from the contribution by the granules. The assumed units may be molecule aggregates or microgel particles, perhaps comparable in diameter to the wavelength of light, but invisible because they are sufficiently highly hydrated that their refractive index is almost the same as the refractive index of the medium. Dehydration by electrolyte reduces the particle size so much that mutual hindrance becomes trifling and the viscosity is correspondingly lowered. Accompanying dehydration is an increase in the refractive index difference between particle and medium, as evidenced by the heightened turbidity of the sol. The kinetic units are much larger than molecules, for solutions of potato amylopectin prepared from sodium starch are considerably less viscous and also less sensitive to the addition of electrolyte than the filtered paste at the same concentration.

In a 0.4% potato starch paste the grundmolarity of the glucose residues is only 0.025 and the concentration of esterified phosphate groups about 10^{-4} *N*. Although locally the concentration may be much higher than 10^{-4} *N*, the phosphate groups are far enough apart that there is little mutual interference with their dissociation tendency, as is shown by the titration curves for potato starch and orthophosphoric acid. Nevertheless, the phosphate ions are apparently close enough to exert appreciable electrostatic repulsion, which has the effect of expanding the amylopectin molecules and promoting their hydration. Cations from even a small concentration of added electrolyte, by clustering around the phosphate ions, neutralize their negative charge and the repulsion is no longer significant. The amylopectin molecules and larger structures of which they form a part are then dehydrated and deswelled, and the paste viscosity is reduced to a few per cent of its value in the absence of added electrolyte.

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SUMMARY

Flow times of potato starch pastes were measured in a single Ostwald viscosimeter made of pyrex glass. Concentrations were 0.4% and 1% and measurements were made at 30 and 90°C. Starches were derived by cation exchange from a high grade commercial potato starch. Under comparable conditions flow times were: "sodium hexametaphosphate" starch, 531 sec.; ammonium starch, 205 sec.; sodium starch, 167 sec.; potassium starch, 136 sec.; calcium starch, 66 sec.; parent commercial starch, 45 sec.; hydrogen starch, 16 sec.; water, 6 sec. The flow time for the potassium starch was reduced to 37 sec. in 10^{-4} *N* KCl; 31 sec. in 10^{-4} *N* CaCl₂ and 13 sec. in 10^{-4} *N* KCl. The curve of pH versus flow time has a high maximum near pH 8.5, the pH of complete ionization of the amylophosphoric acid. Pastes of tapioca and waxy maize starches, which normally are unionized and show no electroviscosity, doubled their viscosity between pH 6 and 10, possibly due to ionization of glucoside hydroxyls. A corresponding effect in potato starch pastes was apparently masked by the ordinary viscosity reduction by the cation of the base used to adjust the pH. Correlation of paste viscosity and starch granule swelling was made through photomicrographs.

Potato starch paste viscosity is related to the ionization of the small content of phosphoric acid esterified with the amylopectin component. Mutual electrostatic repulsion by the ions promotes hydration of the starch and thus increases particle volume and paste viscosity. Factors that decrease the repulsion, such as reduction of phosphoric acid dissociation at low pH, combination of phosphate ions with multivalent cations, or screening of the phosphate ions by cations of added electrolyte, diminish the hydration and paste viscosity.

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